

REPORT  
CD NO.

FOREIGN DOCUMENTS ~~CONFIDENTIAL~~ BROADCASTS

COUNTRY	USSR
SUBJECT	Physics
HOW PUBLISHED	Monthly periodical
WHERE PUBLISHED	Moscow
DATE PUBLISHED	December 1947
LANGUAGE	Russian

DATE OF  
INFORMATION 1947

DATE DIST. 10 Dec 1948

NO. OF PAGES 10

SUPPLEMENT TO

THE FOLLOWING CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF ESPIONAGE ACT 38 U. S. C. 11 AND 12, AS AMENDED. THE TRANSMISSION OR THE REVELATION OF THE CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW. REPRODUCTION OF THIS FORM IS PROHIBITED. MOST OF THE INFORMATION CONTAINED IN MOST OF THE FORM MAY BE UTILIZED AS DECLASS. INFORMATION BY THE RECEIVING AGENCY.

### SOURCE IDENTIFICATION

Investiya Akademii Nauk SSSR, Otdeleniye Tekhnicheskikh Nauk,  
No 12, 1947. (TID Per Abs 57139 -- Translation specifically  
requested.)

## CEMENTATION OF METALS FROM THEIR CHLORIDE SOLUTIONS

D. M. Chizhikov  
B. Ya. Tratsvetlskaya  
Institute of Metallurgy  
imeni A. A. Baykov  
Academy of Sciences USSR  
Submitted 15 July 1947

Tables and figures referred to herein are appended.

The metals which are the objects of our investigation are divided in the order of charge in the following sequences:

Me	Zn	Fe	Sn	Pb	K	Cu
$E_0, \text{B}$	-0.77	-0.44	-0.14	-0.13	0	+0.34

In view of this, it can be expected that tin will displace lead and copper. Tin and iron can be displaced from solutions by zinc.

According to the given order of voltages by Nernst's formula, we find the limiting relation of the concentration to which displacement of one metal by another occurs: (see following page)

213

CLASSIFICATION

**CONFIDENTIAL**

[illegible]

**CONFIDENTIAL**

CONFIDENTIAL

50X1-HUM

Sn - Cu <sup>++</sup> .....	$\lg \frac{C_{Sn}^{++}}{C_{Cu}^{++}} = 16,55$	$\frac{C_{Sn}^{++}}{C_{Cu}^{++}} = 3,56 \cdot 10^{16}$
Sn - Pb <sup>++</sup> .....	$\lg \frac{C_{Sn}^{++}}{C_{Pb}^{++}} = 0,34$	$\frac{C_{Sn}^{++}}{C_{Pb}^{++}} = 2,2$
Zn - Sn <sup>++</sup> .....	$\lg \frac{C_{Zn}^{++}}{C_{Sn}^{++}} = 21,72$	$\frac{C_{Zn}^{++}}{C_{Sn}^{++}} = 5,25 \cdot 10^{21}$
Zn - Fe <sup>++</sup> .....	$\lg \frac{C_{Zn}^{++}}{C_{Fe}^{++}} = 11,38$	$\frac{C_{Zn}^{++}}{C_{Fe}^{++}} = 2,39 \cdot 10^{11}$

From the above-mentioned data it follows that, at the displacement of tin by zinc, copper by tin, and iron by zinc, the process of cementation should go practically to completion. Displacement from a lead solution by tin will occur only at an equilibrium condition when the concentration of tin ions will be about double the concentration of lead ions.

A number of researchers have studied the problems of the mechanics and electrochemistry of the cementation process: N. A. Izgryshev (1), G. V. Akimov (2), and others. The kinetics of the process of displacement of one metal by another has been little studied. V. Mayer (3) studied the kinetics of the displacement of mercury from solutions of its salts by iron and copper.

The purpose of the present work was the study of the kinetics of cementation of metals from their chloride solutions.

#### Experimental Method

To study the reactions,  $Me + H^+$  and  $Me + Me_2^{++}$ , a one-liter glass vessel with a ground lid was used. A four-bladed mixer passed through a central opening in the lid of the vessel, provided with a water seal. Metal discs were placed on the shaft of the mixer, separated from one another by glass washers. Ten discs could be affixed to the mixer at one time.

The upper end of the mixer, during the experiment, was fixed by a clamp to a pulley which was joined by a belt to a motor through a reducing gear. The mixer rotated at 60 rpm.

The cementator was placed in a water thermostat. The water in the thermostat was circulated by the four-bladed mixer. In the heating system there was enclosed a thermo-regulator, connected with a contact thermometer which was situated in the thermostat.

The volume of the reacting solution was 450 ml. Three plates of metal with an over-all surface of 170 sq cm were used in every test. The surface of the plates was first treated with emery cloth, then degreased with an alkali solution, after which it was washed with a weak acid solution and distilled water.

Before the experiment, the temperature of the thermostat was brought to the required value. The investigated solution was heated to this temperature, after which the plates were inserted into the fluid. This moment was considered the beginning of the experiment.

A general view of the apparatus is given in Figure 1. [Photograph not reproduced]

#### 1. Displacement of Hydrogen by Metallic Tin

The experiments of the solutions of tin in hydrochloric acid were conducted at temperatures of 20, 50, and 75°. The first solution contained 10 g/l

2 -  
CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

of HCl. Tests to determine the acidity were made every hour.

The experiments showed that tin is not very soluble in a hydrochloric acid solution. Depending on the temperature and the length of the experiment, the quantity of tin in the final solutions varied from 0.14 to 0.48 g/l (Table 1).

To study the behavior of tin in the solutions which contain  $\text{SnCl}_2$  as well as the hydrochloric acid experiments were conducted on dissolving the metal in solutions which contained 10 g/l of HCl and 62 g/l of Sn. Tests to determine the acidity were made every hour for 6 hours. As the experiments showed, the acidity of the solutions remained almost constant.

## 2. Displacement of Copper by Metallic Tin

The experiments were conducted at temperatures of 20, 30, and 75°. A solution of  $\text{CuCl}_2$  was prepared with three concentrations; with 1.9; 1.0; and 0.5 g/l of Cu. The acidity of all three solutions consisted of 10 g/l of HCl.

Samples were drawn off every 10 minutes for analysis (for the first half hour) and then every 15 minutes.

The results of the experiments are included in Table 2 and Figure 2.

From Table 2 and Figure 2 it follows that, at a temperature of 20° and with an initial concentration of 0.5 g/l of copper, after an hour's cementation in the solution, there remains 0.18 g/l of Cu which is 36 percent of the original quantity. With the increase of initial copper concentration to 1 and 1.9 g/l, the cementation in the course of an hour is more complete, but there still remains 0.06 and 0.013 g/l of Cu, respectively, in solution.

Increasing the temperature to 30° increases the speed of the process. After immersion of the cementation plates in a solution of initial concentration of 0.5 g/l of Cu, there remains, after an hour, 0.01 g/l of copper. Under these conditions the process is also more complete in increasing the concentration of copper in the initial solution to 1 and 1.9 g/l of copper. After an hour in the solution, there remains 0.014 and 0.0028 g/l of Cu respectively.

Increasing the temperature to 75° further increases the speed of the process. With initial concentrations of 0.5 and 1.9 g/l of Cu, 45 minutes after the start of the reaction no copper is found in solution. With an initial concentration of 1 g/l of Cu, the process is complete after 1 hour (Table 2).

Experiments were also conducted on the cementation of copper from solutions containing 30 g/l of tin. The initial concentration of copper in the solutions was 0.92 and 0.38 g/l; acidity was 10 g/l of HCl. The temperature was 75°.

It follows from the data of Table 3 that, under these conditions, also, the process is completed in an hour.

## 3. Displacement of Lead by Metallic Tin

The experiments on the displacement of lead by metallic tin from solutions containing ~0.5 g/l of Pb, were conducted at temperatures of 20, 50, and 75°. The displacement of lead from solutions containing ~1 g/l of Pb were conducted at temperatures of 30 and 75°, and ~2 g/l of Pb, at a temperature of 75°.

The acidity of all the original solutions was 10 g/l of HCl. The length of the experiment was 3 hours. Samples were taken every 30 minutes for analysis.

The results of the experiments are shown in Table 4 and Figure 3 and 4. From the data it follows that, in all cases, the displacement of lead by tin reaches a limit of the relative concentrations of  $\frac{[\text{Sn}^{+2}]}{[\text{Pb}^{+2}]}$  close to 2.2.

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

As is clear from the data of Table 4, the degree of displacement of lead by metallic tin is almost independent of the temperature of the experiment and the initial concentration of lead. Increasing the temperature only hastens the attainment of the equilibrium condition. At a temperature of 20°, the equilibrium occurs after about 2.5 hours; at a temperature of 50°, after 2 hours; at a temperature of 75°, after 1½ hours.

#### 4. Displacement of Hydrogen by Metallic Zinc

Experiments on the solubility of zinc in hydrochloric acid solution were made with initial concentrations of 10 and 20 g/l of HCl at temperatures of 20, 40, and 75°.

Samples for analysis were taken every 15 minutes at high acidity and high temperature. They were made every 30 minutes at low acidity and low temperature.

The results of the tests are shown in Table 5 and Figure 5. From the data of Table 5 and Figure 5 it follows that with the increase in temperature the rate of the reaction  $Zn + 2HCl = ZnCl_2 + H_2$  is increased. If at a temperature of 20° and after 30 minutes of agitation, the acidity has decreased from 10 to 9.42 g/l, then at 40°, the acidity decreased to almost one half as much. At 75° there remained only 0.11 g/l of HCl in solution. When the initial concentration of HCl in the solution is increased, the rate of zinc solubility is also increased somewhat.

#### 5. Displacement of Tin by Zinc

The experiments were conducted at temperatures of 20, 50, and 75°. The amount of tin in the initial solution was 62 g/l. The acidity was 10 g/l of HCl. The duration of the experiments was one hour. Samples for analysis were taken every 10 minutes (during the first half hour) and then every 15 minutes.

A series of experiments was made on the cementation of tin by zinc: (1) from freshly prepared solutions of tin chloride, slightly hydrolyzed but not containing any colloidal sediment; and (2) from solutions of tin chloride which had been standing for several days and which contained a colloidal sediment.

The results of the experiments on the cementation of tin by lead are given in Table 6, and Figure 6.

As is clear from the data of Table 6 and Figure 6 at the cementation of tin from the freshly prepared solutions, the process is fairly complete. One hour from the beginning of the experiment at temperatures of 20° and 50°, there remains in the solution 0.23 g/l Sn; at a temperature of 75° no tin was found. If cementation of tin occurs from solutions containing a suspension of oxybichlorides, then 60 minutes after the commencement of cementation there remains in solution at a temperature of 20°, 14.96 g/l of Sn; at a temperature of 50°, 9.25 g/l of Sn; and at a temperature of 75°, 11.59 g/l of Sn.

The acidity of the solution during cementation of tin by metallic zinc is decreased in all experiments (independent of the temperature), on an average, to ~4 g/l of hydrochloric acid (Table 7, Figure 7).

Comparison of the change of acidity in the process of the displacement of hydrogen ions by metallic zinc in the presence of tin chloride and without it (Figure 8) shows that, at t=20°, the tin ions hasten this process.

At a temperature of 75°, the rate of displacement of hydrogen ions in the presence of tin ions is retarded. This can be explained by the fact that the displacement of tin under these conditions prevails over the displacement of hydrogen.

- 4 -

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL  
CONFIDENTIAL

50X1-HUM

Similar results were obtained with cementation of tin from freshly prepared solutions which contained 376 and 936 g/l of  $\text{SnCl}_2$  (Table 8).

From the data of Table 8 it follows that the cementation of tin is almost complete. With concentrated solutions for speeding the process, it is necessary to remove the film of tin which forms on the zinc.

#### 6. Displacement of Iron by Metallic Zinc

The experiments on the displacement of iron by metallic zinc from a solution of  $\text{FeCl}_2$  were done at temperatures of 20, 50, and 75°.

The experiments lasted 3 hours and samples were taken for analysis every 30 minutes. The concentrations of the initial solutions were:  $\text{FeCl}_2$  - 0.5, 1, and 2 g/l  $\text{Fe}^{++}$ .

The results of the experiments showed that under these conditions precipitation of metallic iron on the zinc did not occur. With a decrease of the acidity from 10 to 3 g/l of  $\text{HCl}$ , the hydrolysis of iron chloride began.

#### Conclusions

1. In a hydrochloric acid solution with a concentration of 10-20 g/l, tin is not very active, whereas zinc readily dissolves in the chloride.
2. Copper can be completely displaced from a solution of its chloride by metallic tin.
3. Lead can only be partly displaced by metallic tin from a solution of its chloride.
4. Tin is practically completely displaced by zinc from freshly prepared solutions of tin chloride.
5. Iron is not displaced by zinc at a concentration of  $\text{Fe}^{++}$  2g/l and below.

#### Bibliography

1. Izmaylov, N. A., Theory and Practice in Displacement of Metals in the Light of Contemporary Electrochemistry, 1938
2. Akinov, G. V., Theory and Methods of Investigating Corrosion of Metals, Pub. AN, SSSR, 1955
3. Major, W., Zeitschr f Elektrochem und angew phys chem, B. 39, 1935

[Appended tables and figures follow.]

- 5 -

CONFIDENTIAL

CONFIDENTIAL

**CONFIDENTIAL**

50X1-HUM

Table 1

**Passage of a Metal Into Solution Due to Action of HCl on Metallic Tin**

Length of Experiment (in hours)	Temperature °C	Quantity of Tin in Solution (Grams/Liter)
22	20	0.2
6	50	0.14
6	75	0.48

Table 2

**Rate of Copper Displacement by Tin, Depending on Initial Concentration and Temperature of Solutions**

Temperature °C	Duration of Experiment in Minutes					
	0	10	20	30	45	60
Change in Amount of Copper in Solution, g/l						
20	0.5	0.46	0.39	0.36	0.34	0.18
	1.0	0.75	0.59	0.39	0.30	0.06
	1.9	1.68	0.96	0.40	0.104	0.013
50	0.5	0.35	0.18	0.040	0.013	0.010
	1.0	0.56	0.24	0.10	0.04	0.014
	1.9	1.28	0.44	0.055	0.024	0.0028
75	0.5	0.25	0.055	0.016	0	0
	1.0	0.49	0.15	0.07	0.05	0
	1.9	1.86	0.08	0.008	0	0

Table 3

Temperature °C	Duration of Experiment in Minutes					
	0	10	20	30	45	60
Change of the Amount of Copper in Solution, g/l						
75	0.38	0.21	0.11	0.04	0	0
	0.92	0.35	0.14	0.02	0.01	0

- 6 -

**CONFIDENTIAL****CONFIDENTIAL**

CONFIDENTIAL

50X1-HUM

Table 4

Rate of Lead Displacement by Metallic Tin Depending on Initial Concentration and Temperature of Solution

Temperature °C	Duration of Experiment in Minutes						$\frac{[Sn^{++}]}{[Pb^{++}]}$
0	30	60	90	120	150		
Change in Amount of Lead in Solution, g/l							
20	0.57	—	0.39	0.39	0.31	0.24	1.7
50	0.57	0.34	0.18	0.18	0.18	—	1.85
	1.13	0.76	0.57	0.52	0.43	—	2.0
	1.31	0.87	—	0.50	0.38	—	2.5
75	0.65	0.37	0.25	0.21	—	—	2.2
	1.29	0.67	0.50	0.44	—	—	2.4
	2.42	1.46	1.00	0.72	—	—	2.4

Table 5

Influence of Temperature and Initial Concentration of Acid on Rate of Displacement of Hydrogen by Metallic Zinc

Temperature °C	Duration of Experiment in Minutes									
	0	15	30	45	60	90	120	150	180	240
Change in Acidity of Solution, g/l										
20	10	9.51	9.42	9.12	—	—	—	—	—	—
40	10	—	5.11	—	1.58	0.29	pH 3.5	pH 4.9	pH 5.9	—
75	10	2.51	0.29	0.11	3.5	—	—	—	—	—
20	20	—	18.25	—	16.28	13.51	10.98	8.91	7.67	6.28
40	20	—	14.45	—	8.40	4.54	1.85	0.66	0.29	—

Table 6

Influence of Temperature on Rate of Tin Displacement by Metallic Zinc

Temperature °C	Duration of Experiment in Minutes					
	0	10	20	30	45	60
Change of Tin Concentration in Solution, g/l From Freshly Prepared Solutions						
20	62	37.6	25.6	15.7	6.54	0.25
30	62	39.2	22.4	15.9	—	0.25
75	54.5	27.5	21.0	6.05	—	None

- 7 -

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

**CONFIDENTIAL**

(Table 6 Contd)

## From Solutions Containing Colloidal Sediment

20	62	49.3	35.9	25.7	17.5	14.96
50	62	40.3	29.8	22.1	14.6	9.25
75	62	43.3	35.6	25.6	16.3	11.59

Table 7

## Influence of Temperature on Acidity Change in Process of Displacing Tin by Zinc

Temperature °C	Duration of Experiment in Minutes					
	0	10	20	30	45	60
Change of Chloride in Solution, g/l From Freshly Prepared Solutions						

20	10	9.01	6.65	5.90	4.42	4.02
50	10	8.77	6.40	5.74	--	3.40
75	10	8.70	6.56	5.66	--	3.12

## From Solutions Containing Colloidal Sediment

20	10	9.16	6.81	6.25	5.38	4.76
50	10	8.85	6.75	6.75	5.82	4.02
75	10	8.95	7.30	7.30	6.07	4.84

Table 8

## Rate of Cementation of Tin by Metallic Zinc From Concentrated Solutions

Solution No 1		Solution No 2	
Duration of Experiment (in minutes)	Change in Amount of $\text{SnCl}_2$ g/l	Duration of Experiment (in minutes)	Change in Amount of $\text{SnCl}_2$ , g/l
0	376	0	556
15	82	15	282
30	4.1	30	250 (Film Removed)
45	0.29	45	10
60	0.15	60	0.30

- 8 -

**CONFIDENTIAL****CONFIDENTIAL**



CONFIDENTIAL

50X1-HUM

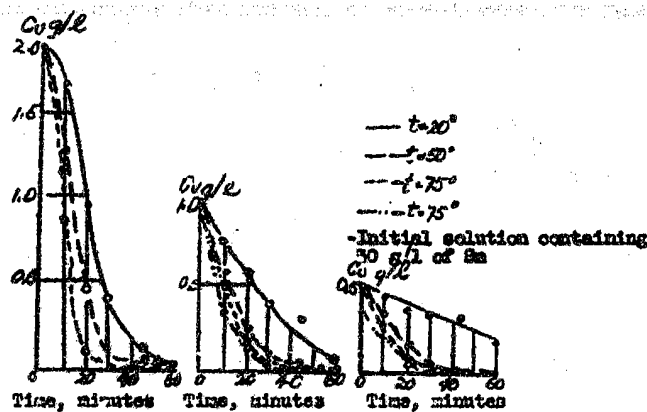


Figure 2. Influence of Temperature and Initial Concentrations of Copper on Rate of Its Displacement by Metallic Tin

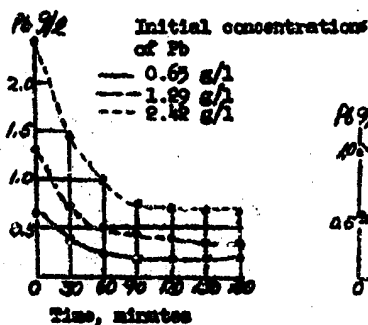


Figure 3. Influence of Initial Lead Concentration on Rate of Its Displacement by Metallic Tin When  $t = 75^\circ$

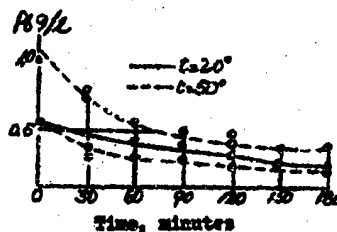


Figure 4. Influence of Temperature on Rate of Lead Displacement by Metallic Tin

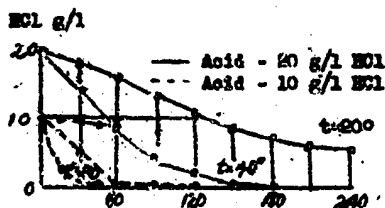


Figure 5. Influence of Temperature and Initial Acid Concentration on Rate of Hydrogen Displacement by Metallic Zinc

- 9 -

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

CONFIDENTIAL

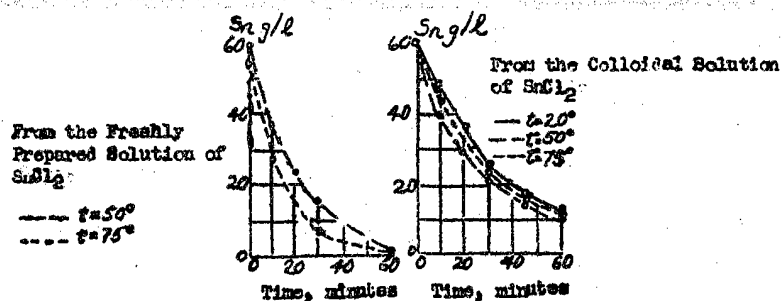


Figure 6. Influence of Temperature on Rate of Displacement of Tin by Metallic Zinc

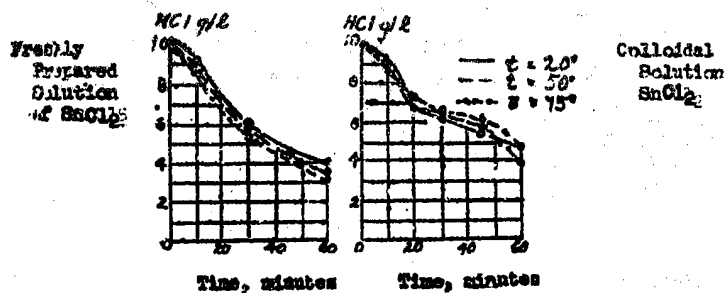


Figure 7. Influence of Temperature on Change of Acidity in Process of Displacing Tin by Zinc

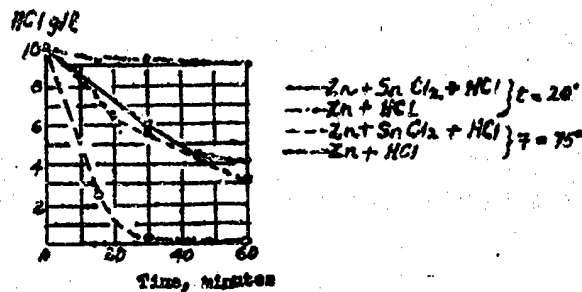


Figure 8. Rate of Hydrogen Displacement by Metallic Zinc in Presence of  $\text{SnCl}_2$  and in the Absence

- B 3 D

- 10 -

CONFIDENTIAL

CONFIDENTIAL